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(54) Title: PARTICLES HAVING SURFACE PROPERTIES AND METHODS OF MAKING THEM (57) Abstract Polymer particles comprising a hydrophobic organic matrix and located at the exterior free cationic groups and a further polymer which comprises free hydroxy groups. The particles are produced by an aqueous suspension polymerisation process wherein the continuous aqueous phase contains a polymerisation stabiliser and a dissolved vinyl addition cationic monomer. The polymerisation stabiliser can be any suitable polymer that comprises free hydroxy groups. The process results in polymers of average particle size in the range 50 to 150 microns and reduced levels of undesired polymer emulsion or undersized particles. The particles are particularly useful for absorbing water insoluble active ingredients, such as insecticides, insect repellents, fragrances, pheromones for subsequent slow release. The cationic surface character of said polymer particles makes them especially useful for forming stable dispersions or slurries in active concentrates such as perfume bases or detergent concentrates. Furthermore these dispersions or slurries remain stable and substantially free of agglomerates. The particles containing active ingredient readily associate with fabrics such as cotton, wool and viscose where the active ingredient is released in a controlled fashion over several days.		

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PARTICLES HAVING SURFACE PROPERTIES
AND METHODS OF MAKING THEM

5 This invention relates to particles having surface properties and methods of making them.

 It is concerned to provide surface properties on the particles that will cause them to be more firmly retained on substrates such as fabrics, vitreous surfaces or the
10 skin. In the invention this is achieved by providing a polymer core to the particle with a surface of a different polymer.

 These particles are particularly suitable for forming a stable-dispersion in a liquid concentrate
15 containing active ingredient, such as a liquid detergent concentrate or liquid rinse conditioner containing a fragrance, wherein the active ingredient becomes imbibed or entrapped within the matrix of the polymer and this provides a product which is suitable for the controlled
20 release of active ingredients.

Summary of the Prior Art

 Various polymer systems have been proposed as diluting systems for active ingredients. WO-A-90/08478
25 relates to food flavouring high note enhancement by micro-bead impregnated with flavouring containing volatiles and is protected by a soluble or swellable coating. This patent describes porous polymeric beads

made from copolymers of divinylbenzene with styrene. The polymeric beads are preferably produced with a coating that retards the release of the flavouring. Illustrative coatings are hydroxyl propyl methyl cellulose and
5 polyvinyl alcohol.

EP-A-297605 is directed to cell culture micro-carriers comprising (meth)acrylic ester polymer particles having positively charged groups on the surface. The polymer particles have an average diameter of between 100
10 and 1000 microns and are prepared by oil in water type suspension polymerisation of (meth) acrylic ester as a monomer followed by treating the resulting polymer particles with ammonia or amine having 5 or less carbon atoms. Typically polyvinyl alcohol may be used as a
15 stabiliser in the aqueous phase of the polymer. The positive groups are generated by reacting the formed polymer particles with the amine or ammonia. In order for this to be possible it is necessary that the matrix monomer contains functional groups that react with the
20 ammonia or amino compounds, e.g. glycidyl methacrylate.

JP-A-62289238 describes resistant anion exchangers. This patent describes an anionic exchange resin produced by polymerising glycidyl esters with other vinyl
compounds and then reacting the polymer particles with
25 ammonia or amines.

WO-A-92/18222 describes the preparation and use of solid non-porous crosslinked polymer beads. The beads are produced by first forming a monomer phase which

comprises at least one monoethylenically unsaturated monomer and a monomer soluble initiator. The monomer phase is then combined with an aqueous liquid-phase which is substantially immiscible with the monomer phase to form a reaction mixture. An organic polymer colloid suspending agent can also be combined with the aqueous phase. Preferred suspending agents include polyvinyl polyols having a molecular weight of at least 40,000 and includes polyvinyl alcohol.

10 US-A-4842761 discloses composite particles comprising a water soluble polymer and a water insoluble polymer. Discrete entities of one polymer are embedded within a matrix of the other polymer. The composite particles are used as perfume carriers in laundry
15 detergents and provide controlled release perfume.

GB-A-2234901 describes a method of encapsulating a water insoluble substance, such as an insecticide, within a carrier capsule. The water insoluble substance is dissolved in a substance which is capable of modifying
20 the carrier capsule so that it imbibes said substance and then entrapping said substance within the thereby modified carrier capsule by removal of the carrier capsule modifying agent. The patent exemplifies starch granules and cellulosic fibres as carrier capsule.

25 EP-A-285694 is one of a series of documents concerned with porous cross linked polymers obtained by polymerisation around droplets of a liquid substance which may subsequently be removed. These porous polymers

can act as carriers for a variety of liquids. They are used in products for application to the skin, and give controlled release of the liquid to the skin.

5 The invention

We have now found that the properties of polymer particles - which are insoluble in water - for controlled retention and/or release systems can be improved by providing at the surface of the insoluble particles which
10 are preferably formed from a (meth) acrylic monomer with at least three carbon atoms in the esterifying alcohol, a further polymer with free hydroxyl groups. Such polymer enhances deposition of the particles on substrates. The use of such particles can enhance deposition of perfume
15 or other active ingredients.

The present invention may also provide particles containing an organic polymer core, which are insoluble in water, characterised in that the particles have at their exterior, a different polymer or polymers which
20 provide(s) hydroxy functionality and cationic functionality. There may be a single such different polymer providing both those functionalities.

The cationic functionality may be provided by pendant cationic groups that have been derived from
25 cationic vinyl addition monomer units bonded to the organic water insoluble polymer or cationic monomer units present in the further free hydroxy containing polymer.

The present invention also provides organic polymer

particles of average particle size at least 40 microns,
which have been produced by a process of suspension
polymerisation of organic water insoluble vinyl addition
monomers in an aqueous medium comprising a hydroxy
5 containing polymeric polymerisation stabiliser that has
free hydroxy groups, characterised in that a cationic
monomer containing a C₄-C₈ alkyl, aryl, alkaryl or aralkyl
pendant groups are also present in the aqueous medium and
this cationic monomer becomes incorporated onto the
10 exterior of the polymer particles during the
polymerisation process.

The polymer particles of this invention are
particularly suitable as carriers of active substances,
especially those used in controlled release systems. The
15 polymer particles can be dispersed into a liquid
concentrate, such as a detergent concentrate or rinse
conditioner containing an active ingredient such as a
fragrance, so that the active ingredient is imbibed by
the polymer particles and becomes entrapped within the
20 polymer matrix. It is important that the particles
remain in suspension in the active concentrate and do not
agglomerate. The surface cationic character of the
particles help stabilise the particles from agglomeration
in the active concentrate, especially when such a liquid
25 is an aqueous concentrated fabric conditioning agent.

Surprisingly it has been found that the presence of
the functionalities at the exterior of the particles
enhances the deposition of the particles onto certain

substrates such as fabrics, skin etc. and thereby enhances the delivery of the active ingredient in a controlled fashion. An example of this could be a fabric treatment formulation that contains said particles, in which the active ingredient is an insecticide or insect repellent. The particles have a strong affinity for the fabric due to the hydroxy groups and possibly also by the cationic groups present at the exterior of the polymer particles. The polymer particles release insecticide for a prolonged period thereby preventing the damage to the fabric by insect grubs. The polymer particles also have the advantage of being easily removed from the substrate if required by normal laundering.

The hydrophobic monomer or monomer blend comprises a monoolefinic monomer such as (meth) acrylic esters optionally with other monomers such as styrene and optionally a polyolefinic monomer capable of crosslinking the hydrophobic monomer. In one preferred embodiment the hydrophobic monomer mixture comprises isobutyl methacrylate with 2 mole % divinyl benzene.

The cationic vinyl addition monomer is typically a vinyl addition compound that incorporates a quaternary ammonium group and contains a C_4 - C_8 alkyl, aryl, aralkyl or alkaryl pendant group. Typically this can be a C_4 - C_8 halide quaternised dimethylamino ethyl(meth)acrylate. A preferred cationic monomer for this invention is benzyl chloride quaternised dimethylaminoethyl acrylate ("MADQUAT"). The presence of cationic monomer may also

increase particle size in the product, in a direct relationship between amount of cationic monomer and average size.

The hydroxy polymeric polymerisation stabiliser which eventually becomes incorporated onto the exterior of the organic polymer particles can be any polyhydroxy compound suitable as a polymerisation stabiliser. Typically this can be a polyvinyl alcohol or a cellulosic ester. Polyvinyl alcohols are derived from the hydrolysis of polyvinyl acetate. Different grades of polyvinyl alcohol with different degrees of conversion can be formed depending on how much of the original hydrophobic character needs to be retained. For the purposes of this invention at least 80%, more preferably at least 90% of the vinyl acetate units should have been converted into vinyl alcohol units.

It may also be possible to impart some or all of the cationic functionality to the final polymeric particles by incorporating cationic monomer units into the polyhydroxy polymer. One example of this would be to first provide a copolymer of vinyl acetate with vinyl acetamide and then hydrolyse this to a polymer which would then have vinyl alcohol units and vinyl amine units. The vinyl amine units can be rendered cationic by subsequent protonation.

The particles themselves are insoluble in water, so that they can be deposited from an aqueous wash or rinse liquor.

The functional polymer at the exterior of these particles may form, or be included within a coating or incomplete coating on these individual particles. The hydroxy functional polymer is preferably nonionic or cationic. It will be explained below that it generally constitutes between 1 and 25% of the weight of the perfume-containing particles, usually between 1 and 10%.

Particle size

10 Polymer particles of this invention desirably have an average particle size of at least $10\mu\text{m}$, better at least $20\mu\text{m}$ or $30\mu\text{m}$, even better at least $40\mu\text{m}$, for ease of handling. The rate of release of any active ingredient in the particles may be faster than desired if the particles are of very small size such as average size of $1\mu\text{m}$. The polymer particles desirably have an average size not larger than $150\mu\text{m}$, better not over $125\mu\text{m}$ so that the particles are not easily visible after deposition.

For particles intended to be used in fabric washing or conditioning, it is especially preferred to use particles with a mean size of at least $40\mu\text{m}$, e.g. 40 to $100\mu\text{m}$.

For particles intended for other products, e.g. personal washing products, a faster rate of release may be desired than with fabrics products, although retention and delay in release for some hours is still desirable, consequently a smaller particle size may be advantageous, such as a mean size in the range from 10 to $50\mu\text{m}$.

Polymerisation techniques generally produce a range of particle sizes. For this invention it is desirable that a high proportion of the particles lie between the above limits on particle size. Thus, when particles are
5 intended for fabric treatment, preferably 90% or more of the particles are larger than $30\mu\text{m}$. Preferably also 90% or more of the particles are not larger than 150 or even 125μ . Better, 95% or more are not larger than 125 or even $100\mu\text{m}$.

10 To achieve these criteria, it may be necessary to sieve the particles and thereby separate oversized and/or undersized particles. An important aspect of reducing the amount of emulsion polymer formed (broadly speaking, polymer beads of a size below $10\mu\text{m}$) is to use an
15 initiator system that is substantially insoluble in the aqueous phase, so as to prevent initiation of monomer molecules held in micelles. Suitable water insoluble initiators include azo compounds such as azobisisobutyronitrile (AIBN) and higher alkyl peroxides.

20

Hydroxy functional polymer

This polymer bearing hydroxy groups and located at the exterior of the particles serves to enhance deposition onto (or retention on) skin, hair, hard
25 surfaces especially vitreous surfaces and fabric.

This polymer is desirably such that at least 80% of the monomer residues in the polymer contain at least one free hydroxy group able to participate in hydrogen

bonding. The polymer is preferably nonionic and such that, in its pure state, it is water-soluble. However, when attached to the exterior of the particles, it does not render them water soluble. It is attached in such a way that it is not washed off completely upon contact with water. In some instances there may be chemical bonding, even in a form of grafting.

The preferred polymer is polyvinyl alcohol.

As is well known, polyvinyl alcohol cannot be prepared directly by polymerisation, and is obtained by the hydrolysis of polyvinyl acetate. This hydrolysis generally stops before completion, and polymers with varying amounts of hydrolysis are commercially available.

We have found that deposition of particles, especially onto fabric, is better when the polyvinyl alcohol exhibits a substantial level of hydrolysis.

We may therefore prefer to use polyvinyl alcohol which is 85 to 100% hydrolysed i.e. in which 85 or 88 to 100% of the acetate residues have been removed by hydrolysis. More preferably, the polyvinyl alcohol is at least 90% better at least 96% hydrolysed, e.g. 96 to 99% hydrolysed.

Another possible polymer is a copolymer of polyvinyl alcohol, available through hydrolysis of the corresponding copolymer of vinyl acetate. For example a copolymer of vinyl acetate and vinyl formamide, with a high proportion of vinyl acetate can be hydrolysed to a copolymer of vinyl alcohol and vinyl formamide. Further

hydrolysis of such a polymer converts the formamide residues to amine groups, giving a cationic copolymer of vinyl alcohol and vinyl amine.

Another category of polymers which can be used is
5 cellulose and chemically modified cellulose where the modification does not greatly reduce the number of hydroxyl groups present. Examples of polymers in this category are hydroxyethyl cellulose, and hydroxypropyl cellulose.

10 Hydroxyethyl cellulose is available commercially and is made by treatment of cellulose with sodium hydroxide, followed by reaction with ethylene oxide. Another possibility is cellulose which has been chemically modified by the introduction of cationic substituent
15 groups.

It is a characteristic of many grades of polyvinyl alcohol and of hydroxy ethyl cellulose that free hydroxy groups constitute more than 20%, often more than 25% of the weight of the polymer.

20

Solid particles

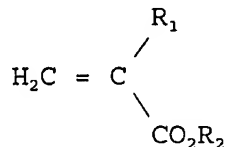
For this invention it is preferred to use polymer particles which are solid - although they may be porous as well as solid - rather than particles in the form of
25 hollow capsules.

Advantages of solid particles are that the desired size range is accessible, and that the polymerisation reaction can be carried out in the absence of perfume.

The particles could possibly be porous particles made by polymerisation around a liquid pore-forming agent, as taught in EP-A-285694. However, we have found it to be unnecessary to include such a pore-forming agent. Polymers formed by simple polymerisation of a monomer mixture are able to absorb and carry active ingredients.

Preferred polymer particles may be formed by the polymerisation of vinyl monomers, with some cross linking and/or chain branching agent included in the monomers which are polymerised, so that some cross links are formed between the polymer chains. If a cross linking agent is used, the proportion of cross linking may be low, so that after polymerisation there may be some polymer chains which remain entirely linear and are not cross linked to any other chains.

A number of vinyl monomers containing a single carbon-carbon double bond may be used. One suitable category of monomers is the esters of acrylic and alkyl acrylic acids, of formula



where R_1 is hydrogen or alkyl of 1 to 6 carbon atoms, preferably 1 to 3 carbon atoms and R_2 is alkyl (including branched and cycloalkyl) of 1 to 7 or 8 carbon atoms, preferably 3 or 4 carbon atoms in a straight or branched chain, or 7 carbon atoms in a bridged ring.

Specific examples of suitable monomers are isobutyl methacrylate (which is particularly preferred), n-butyl (meth)acrylate, isobutyl acrylate, n-propyl acrylate, iso-propylmethacrylate and norbornyl (meth)acrylate.

5 Less preferred is methyl methacrylate.

Another suitable monomer is styrene.

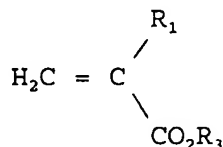
It is possible to use simple linear polymers.

However, these can give particles which are somewhat sticky, and it is usually convenient to introduce some
10 cross-linking or chain branching.

Cross linking between polymer chains formed from the above monomers can be achieved by including in the monomer mixture a small proportion of a monomer with two carbon-carbon double bonds, often termed polyolefinic or
15 multifunctional cross-linking monomers. The use of such a material to provide cross linking is well known in other applications of polymers, although it is usual to introduce a greater proportion of cross linking than is required for this invention. Examples of this type of
20 cross linking agent are divinyl benzene, diesters formed between acrylic acid and diols and higher ester formed between acrylic acid and polyols - which may be sugars.

Chain branching can be introduced by including among the monomers a hydroxyalkyl monomer of formula

25



30 where R_1 is as specified above and R_3 is alkyl of 1 to 6

carbon atoms bearing at least one hydroxy group, preferably 3 to 4 carbon atoms in a straight or branched chain and bearing a single hydroxy group. These monomers undergo a side reaction during the course of

5 polymerisation, and this side reaction produces chain branching. When there is chain branching without cross linking, it is suitable that hydroxyalkyl monomer of the above formula provides from 10 to 40% by weight of the monomer mixture.

10 Suitable hydroxyalkyl acrylate monomers are hydroxypropyl methacrylate, hydroxybutylacrylate, and hydroxyethylacrylate.

Attachment of a polymer with hydroxy groups, notably polyvinyl alcohol, at the exterior of the particles, can
15 be achieved by polymerising the monomers in the presence of the polyvinyl alcohol (or other polymer with hydroxy groups) using the technique of suspension polymerisation.

Suspension polymerisation

20 Suspension polymerisation is a process in which the organic monomers are formed into a suspension in an aqueous phase, and polymerised. Polymerisation of each suspended droplet leads to a bead of polymer.

During the polymerisation process droplets of
25 polymerising monomer and polymer particles are constantly moving through the continuous suspension liquid and statistically there is a high probability of collisions between droplets and between particles. It is important

that agglomeration of particles is prevented as this could very quickly result in loss of stability during the polymerisation. It is customary to stabilise the suspension by incorporating a stabilising agent in the aqueous phase before adding the monomer. Polyvinyl alcohol (PVA) is known to act as a stabiliser.

Polymerisation may be carried out using a combination of PVA and second stabilising agent which may or may not be a second hydroxy polymer. It is quite feasible to use a mixture of PVA grades. Examples of materials which can be used as second stabilisation agents include other water soluble polymers such as polyacrylic acid or water soluble salts thereof. Typically the amount of stabiliser used is generally between 1 and 5% by weight of aqueous phase or 3 to 15% by weight of the monomer being polymerised, most preferably between 5 and 10% by weight of monomer.

It is possible to incorporate surfactants such as sodium oleate or sodium lauryl sulphate into the continuous aqueous phase to assist with the stabilisation of the dispersed phase monomer droplets during the polymerisation. Typically the surfactants used in this application are those which are preferentially soluble in the aqueous phase, typically surfactants which have an HLB of 8 or above. However, when choosing a surfactant in this invention it is important that it does not have an adverse effect on the droplet size and could result in the formation of unacceptably small sized polymer

particles. It is particularly important to reduce the levels of emulsified droplets, which give rise to polymer particles below 10 microns. It is desirable to reduce the levels of emulsion to below 10%, particularly below 5 8%.

Thus, a typical polymerisation procedure will commence by forming an aqueous solution of the hydroxy functional polymer which acts as stabilising agent, together with a polymerisation initiator, in a reaction 10 vessel. Then while agitating the contents of the reaction vessel, the organic monomers are progressively fed in so that the monomers become dispersed in the aqueous phase and polymerise therein. The addition of monomers can be continued until the mixture in the 15 reaction vessel is a slurry of polymer beads containing about 30% by weight of polymer.

In a possible variation of this procedure some of the monomer is dispersed in the aqueous solution of stabilising agent before any polymerisation initiator is 20 added. In another possible variation the monomers are emulsified in water before they are added to the reaction vessel.

Suspension polymerisation typically produces polymer beads with a diameter larger than 100μ . Smaller particle 25 sizes in the range of $50-100\mu$ can be obtained by increasing the amount of stabiliser in the aqueous phase, or by increasing the amount of agitation, or both.

Further examples of materials which can serve as a

second stabilising agent include sodium oleate and sodium lauryl sulphate, both of which are anionic surfactants, also nonionic surfactants with HLB of 8 and above, such as C₁₃/C₁₅ alcohol ethoxylated with 3 to 11 ethylene oxide residues, and sorbitan ester surfactants of similar HLB.

The amount of hydroxy functional polymer present in solution as a stabilising agent will generally be between 1% and 5% by weight of the aqueous phase in which polymerisation occurs. Larger amounts can also be used.

The amount may well be between 3% and 15% by weight of the monomers undergoing polymerisation, possibly between 5% and 10%.

Observation by microscopy of such particles showed the hydroxy functional polymer to form a coating or incomplete coating of the particles, from which it can be estimated that the amount of hydroxy functional polymer attached to the particles was at least 1% by weight of these particles after (and also of course before) the incorporation of perfume.

Cross-linking

Cross-linking between polymer chains formed from the above monomers can be achieved by including in the monomer mixture a proportion of a monomer with two or more carbon to carbon double bonds, often termed polyolefinic or multifunctional cross-linking monomers. The use of such polyolefinic monomers to provide cross-linking is well known in the application of polymers. In

generally, as the degree of cross-linking increases the ability for a polymer to swell in solvents decreases but the rigidity and glass temperature increases. In some applications such as synthetic rubber the rigidity and durability of the polymer are important characteristics and so the degree of cross-linking would be high.

The properties of the beads produced by suspension polymerisation can be influenced by the degree of cross-linking. As mentioned previously a function of the polymerisation stabiliser is to prevent the agglomeration of polymerising particles. During the polymerisation process the cross-linking monomer becomes incorporated causing cross-linking between polymer chains to form a three dimensional network. Cross-linking results in the surface properties of the polymerising beads being much less sticky and much less prone to agglomeration when collisions occur.

In this invention it is important that the polymer can swell sufficiently in the liquid medium that comprises active material to allow said active material to penetrate the polymer particles but important that the polymer matrix retains its form and does not dissolve. The amount of cross-linking is much lower than say for synthetic rubber. Generally a suitable amount of cross-linking agent for this invention is not over 5 mole % of the monomer mixture and is preferably in the range from 0.5 to 3 mole %.

It is important that the polyolefinic monomer is

soluble in or miscible with the hydrophobic monoolefinic monomer used and that the reactivity ratios are such that the polyolefinic monomer will readily copolymerise with the hydrophobic monoolefinic monomer. Examples of

5 polyolefinic monomers used as cross-linking agents include divinyl benzene and diesters of acrylic acid or methacrylic acid with diols and diesters or higher esters formed between two or more moles of acrylic acid or methacrylic acid and polyols for example polyethylene

10 glycol diacrylate.

Hydroxy substituted acrylate esters can also lead to cross-linking. The mechanism by which they do so is a side reaction which is not fully understood. When used, a suitable amount may lie in a range from 3 to 30 mole%

15 of the monomer mixture. Preferably 10 to 30 mole%.

After the manufacture of the particles by polymerisation, the direct product is in the form of an aqueous slurry. If desired, the particles may be separated from the aqueous phase by filtration or

20 centrifuging, possibly followed by drying.

Another possible route for the production of polymer particles is emulsion polymerisation to yield an aqueous emulsion of very small polymer particles (typically of sub-micron size) followed by a drying step to agglomerate

25 these particles into larger particles with a size of at least 20μ .

Absorption of perfume by the particles can be brought about simply by bringing the perfume and the

particles into contact, and allowing them to stand. This may be done by mixing perfume with the particles after they have been separated from the aqueous phase, or it may be done by mixing perfume into an aqueous slurry of the particles and allowing the mixture to equilibrate. It can be done by mixing the particles and perfume separately into an aqueous liquid product and allowing that mixture to equilibrate.

10 Encapsulated particles

A further possibility is to encapsulate a "core" of polymer as described above, with aminoplast resin, while providing hydroxy-functional polymer at the exterior of the capsules, and absorb perfume within the core.

15 Several typical procedures are available to produce such encapsulated polymer. One procedure is to form polymer beads, for example of an acrylate polymer, as described earlier, and dispense this organic mixture in an aqueous solution containing the hydroxy functional polymer and urea-formaldehyde precondensate. The mixture is agitated to keep the organic mixture in suspension. While maintaining solution temperature between 20°C and 90°C, acid is then added to catalyse polymerisation of the dissolved urea-formaldehyde precondensate. If the solution is rapidly agitated during this polymerisation step, shells of water-insoluble, urea-formaldehyde polymer form around and encapsulate the dispersed organic mixture and molecules of the hydroxy-group containing

polymer are incorporated in and at the exterior of these shells. Melanine-formaldehyde precondensate can be used in place of urea-formaldehyde, and may be preferred.

Another procedure is to form encapsulated core polymer, in the absence of perfume, and subsequently allow perfume to diffuse through the shell, into the core polymer. We have found that absorption of perfume is possible through a thin shell, even though a thicker hollow shell is capable of retaining liquid perfume. Suitably the weight of polymer forming the shell is less than the weight of polymer forming the core, and the shell to core weight ratio may lie in a range from 1:3 to 1:20, better 1:5 to 1:20.

Hydroxy functional polymer will generally provide a substantial proportion of the shell, yet constitute from 1% to 25% of the capsules.

For this procedure it has been found preferable to encapsulate monomer within an aminoplast shell, then polymerise the monomer to form a (preferably solid) core of polymer within the shell. Less preferred is to partially polymerise the core before encapsulation.

It is also possible to encapsulate a mixture of liquid monomer and fragrance, then polymerise. However, this necessarily exposes perfume to the polymerisation reaction, whereas absorption of perfume through the shell into a previously polymerised core does not.

When a product contains particles in which perfume is absorbed within polymer which is encapsulated by a

thin shell, perfume can diffuse through the shell, and can be released without rupture of the shell, although the release and dispersion of perfume will be slower than for neat perfume. Thus, encapsulated polymer with
5 absorbed perfume can provide deposition and retarded release of perfume similarly to the (preferred) arrangement when perfume is absorbed in polymer beads which have hydroxy functional polymer directly at their exterior.

10 Examples of preparation and use of the particles will now be given.

Example 1

A 700ml reaction flask equipped with motorised
15 stirrer, reflux condenser, thermometer and inlet tube for delivery from a peristaltic pump was placed in a water bath at about 65°C.

An aqueous phase was prepared by mixing hydroxyethyl cellulose (5 parts) and deionized water (168 parts). The
20 hydroxyethyl cellulose had a degree of substitution of one and was available from Hercules Chemical Corp as NATROSOL 250L. This phase was mixed until the hydroxyethyl cellulose dissolved and was then charged into the reaction flask. Stirring was applied to the
25 reaction flask.

A monomer phase was prepared by mixing iso-butyl methacrylate (70 parts) with a cross linking co-monomer which was 1,6-hexanedioldiacrylate (1.8 parts).

2,2'-azo(bis)isobutyronitrile [usually abbreviated to AIBN] (2 parts) was added directly to the reaction flask and dispersed for about five minutes.

The monomer phase was added to the stirring reaction
5 flask using a peristaltic pump over about ninety minutes. After addition the reaction mass was stirred at about 65°C for about three hours and subsequently cooled.

The polymer beads were recovered from the aqueous slurry by filtration and air dried. The beads were
10 sieved to separate the fraction with size below 125 μ m.

It can be seen that in this Example, the total quantity of hydroxy-functional polymer was less than 10% by weight of monomers, and only part of that quantity becomes attached to the polymer beads.

15 The cross linking agent is 2% by weight and 1.63% by mole of the monomer mixture.

Example 2

A 700ml reaction flask, equipped as in Example 1,
20 was placed in a water bath at about 65°C.

An aqueous phase was prepared by mixing poly(vinyl alcohol) available as Gohsenol AH-22 from Nippon Gohsei British Trades and Shippers Ltd, Dagenham, Essex and having a degree of hydrolysis of 97 to 98.8% (5 parts)
25 and deionized water (168 parts). This phase was stirred until the poly(vinyl alcohol) dissolved and was then charged into the reaction flask. Stirring was applied to the reaction flask.

A monomer phase was prepared by mixing styrene (68 parts) and 1,6-hexanedioldiacrylate (1.8 parts).

AIBN (2 parts) was added directly to the reaction flask and dispersed for about five minutes.

5 The monomer phase was added to the stirring reaction flask using a peristaltic pump over about ninety minutes. After addition the reaction mass was stirred at about 65°C for about three hours and subsequently cooled.

10 At this stage, the products was in the form of an aqueous slurry from which the polymer beads were recovered by filtration and air dried.

Examples 3 to 5

15 The procedure of Example 2 was repeated with different monomers as follows:

Example 3: Methyl methacrylate (70 parts) and
1,6-hexanedioldiacrylate (1.8 parts)

Example 4: n-Butylmethacrylate (70¹ parts) and
1,6-hexanedioldiacrylate (1.8 parts)

Example 5: iso-butylmethacrylate (54 parts) and
hydroxypropylmethacrylate (18 parts)

20

In each of these examples the monomers were satisfactorily converted to polymer beads. These were recovered by filtration and air dried.

25 Example 6

Beads, produced as in Example 5, were sieved to remove any beads larger than 75 μ m diameter.

A perfume was prepared consisting of equal amounts of

- i) dihydromyrcenol (2,6-dimethyl-7-octen-2-ol)
- 5 ii) anisaldehyde
- iii) dimethylbenzylcarbinyl acetate
- (iv) 1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4-tetrahydronaphthalene, available under the trademark "TONALID",
- 10 (v) 3a,4,5,6,7,7a-hexahydro-4,7-methano-1(3)H-inden-6-ylpropionate, available under the trademark "FLOROCYCLENE",

Perfume-loaded polymer beads were prepared by mixing
15 the above beads and perfume into a diluted rinse conditioner, to yield an aqueous slurry containing:-

	Polymer beads	10.71%
	Perfume	10.71%
20	Dihardened tallow dimethyl ammonium chloride	3.5%
	Water	Balance

This slurry was agitated for two hours and left to
25 stand for twenty four hours, after which it appeared that all the perfume had been absorbed into the polymer beads.

This slurry was added to a quantity of a rinse conditioner formulation which was an aqueous emulsion

containing a 1,2-dihardened tallowloxy-3-trimethyl ammoniopropene chloride (HTTMAPC) as cationic softener. This material is disclosed in US-A-4137180.

5 The formulation contained:

	HTTMAPC (including some fatty acid impurity)	13.5%
	Ethoxylated Coconut alcohol (20EO)	0.75%
10	Hardened tallow alcohol	0.75%
	Calcium chloride	0.2%
	Preservative	0.02%
	Demineralised water	Balance to 100%

15 After adding the slurry, the resulting perfumed formulation contained 0.75% by weight perfume, carried in polymer beads. The perfumed rinse conditioner formulation was agitated for two hours and then stored for six days in a closed container. A control
20 formulation contained 0.75% by weight perfume, and the same concentration of fabric softener, without polymer beads.

To test perfume deposition, this rinse conditioner formulation and the control formulation were both diluted
25 with water to provide rinse liquors containing 0.5% of the rinse conditioner formulation.

Test pieces of fabric were de-sized cotton terry towelling, approximate weight 25g. For each test, a piece of terry towelling was weighed accurately and

treated with 30 times its own weight of rinse liquor, in a Tergotometer pot, stirring at 80rpm for 20 minutes. The cloth was then wrung out by hand, and line dried.

The amount of perfume in the fresh and used rinse
5 liquors was determined by solvent extraction from 100g of rinse liquor and gas chromatographic (GC) analysis of the solvent extract. The percentage deposition of perfume materials onto the cloth was calculated for three of the five materials. The results obtained were:

10

Ingredient	% Deposition	
	Control	Perfume in polymer beads
Dihydromyrcenol	14	25
DMBCA	24	33
15 Florocyclene	38	42

The amount of perfume on the dry cloth was determined by extraction of 5g of dry cloth with 20ml
20 ethyl acetate, followed by GC analysis of the solvent extract.

The amount of perfume detected was expressed as a percentage of the theoretical maximum quantity (which would be present if there were complete deposition onto
25 fabric and no subsequent losses).

The results obtained for materials were:

Ingredient	% Ingredient remaining on dry cloth	
	Control	Perfume in polymer beads
Dihydromyrcenol	not detected	1.3
DMBCA	not detected	8.0
Florocyclene	not detected	9.8
Tonalid 2	30.2*	51.1*

* = result possibly affected by other GC peaks.

Example 7

Perfume mixture was incorporated into polymer beads, as set out in the previous Example, but with two ratios of polymer to perfume. These were 1:1 polymer to perfume and 1:2 polymer to perfume.

The resulting perfumed beads were incorporated into rinse conditioner formulations as in the previous example so as to provide 0.75% by weight perfume in each formulation. A control formulation contained 0.75% by weight perfume, but no polymer. These were diluted to rinse liquors containing 0.5% by weight fabric conditioner, and used to treat terry towelling as in the previous Example.

The treated cloths were assessed by a panel of eight people.

Assessments were made on damp cloth directly after treatment, on dry cloth 24 hours after treatment and on dry cloth five days after treatment.

The assessments were:

Assessment Stage	Control (no polymer)	1:1 polymer to perfume	1:2 polymer to perfume
Damp Cloth	Strongest	Weaker than control Equal to (1:2)	Weaker than control Equal to (1:1)
5 Dry Cloth (24 hours)	Intense Tonalid odour	Florocyclene, Tonalid and anisaldehyde odours Stronger than (1:2)	Florocyclene, Tonalid and anisaldehyde odours Weaker than (1:1)
Dry Cloth (five days)	Tonalid odour	Florocyclene, Tonalid and anisaldehyde odours Weaker than (1:2)	Florocyclene, Tonalid and anisaldehyde odours Stronger than (1:1)

10

Example 8

Beads were produced as in Example 2. The monomer mixture was isobutyl methacrylate (70 parts) mixed with 1,6-hexanedioldiacrylate (1.8 parts). Preparations were

15 carried out using various different grades of polyvinyl alcohol and some other materials as the stabiliser. The grades of polyvinyl alcohol differed in the extent to which they had been hydrolysed from polyvinyl acetate.

20 The materials used were:

	Stabiliser	Hydrolysis	Tradename
A	polyvinyl alcohol	98-99%	Gohsenol N-300
B	polyvinyl alcohol	97-98.5%	Gohsenol A-300
C	polyvinyl alcohol	87-89%	Gohsenol GH-23
25 D	polyvinyl alcohol	78-80%	Gohsenol KH-17
E	polyvinyl alcohol jointly with a surface active acrylamide copolymer	97-99%	Gohsenol AH-22

F	polyvinyl alcohol jointly with a 95:5 copolymer of acrylamide and behenyl (25 ethylene oxide) methacrylate	97-99%	Gohsenol AH-22
G	hydroxyethyl-cellulose		Natrosol 250L
H	surface active acrylamide copolymer (comparative example)		MER 10

5

In all cases the dried beads were mixed with their own weight of a single perfumery material, Florocyclene, also used in Example 6. After mixing they were left to equilibrate overnight, then a small quantity of finely
10 divided silica (2% based on the total weight of perfume and polymer) was added as a surface improving flow aid.

The perfume-containing polymer beads were mixed into rinse conditioner (as used in Example 6) using a magnetic stirrer. In each case the amount of perfume carrying
15 beads was 1.5% by weight of the rinse conditioner, so that the quantity of perfume was 0.75% by weight of the rinse conditioner formulation. A control formulation was prepared containing 0.75% Florocyclene without the polymer.

20 Deposition onto fabric was assessed using test cloths made of cotton terry towelling, acrylic fabric, and polyester. The fabric washing procedure was the same as set out in Example 6. After treatment of the fabric and drying, the intensity of Florocyclene on groups of
25 the dried test cloths was assessed by a panel of five

assessors who ranked the cloths in order of intensity of Florocyclene. The following results were obtained as unanimous views of the assessors:

- 5 On cotton test pieces B>A>C>Control
 C>D>Control
 E>F>Control
 and G>H>Control
 On acrylic test pieces A>B>C>Control

10

On polyester test pieces A,B and C were all stronger than the control, but the assessors were not unanimous as to which of the three gave the highest perfume intensity.

- These results demonstrate that the polymer particles
15 A,B,C and D made using polyvinyl alcohol as stabiliser and hydroxy-functional monomer all gave an increase in the perceived intensity of perfume on fabric. So did polymer particles E and F made using polyvinyl alcohol in a mixture of stabilisers. The polymer particles G made
20 using hydroxyethylcellulose as stabiliser and hydroxy-functional monomer also gave an increase in the perceived intensity of perfume on fabric and were superior to the particles H made using a different polymer as stabiliser.

25 Example 7

942 parts of water, 1228 parts of a 10% solution of 88% converted polyvinyl alcohol, 4 parts benzyl chloride quaternised dimethylaminoethyl methacrylate (MADQUAT) and

6 parts Tegofoamex defoamer were charged to a round
bottomed reactor vessel. The stirrer was started at
150rpm and a nitrogen bleed was applied and the contents
of the vessel were warmed to between 60 and 62°C. 12.3
5 parts of Vaso 67 thermal initiator slurried in 36 parts
of water was then added to the contents of the vessel. A
monomer blend comprising 1225 parts of isobutyl
methacrylate and 24.5 parts butane diol diacrylate were
then charged to the reactor over 1 hour to provide
10 reaction solids of 35%. The temperature of the reaction
needed was held at 60 - 62°C until monomer addition was
completed and then the temperature of the was allowed to
rise under the reaction exotherm to 80°C where it was
held for 3 hours. The reaction medium was then cooled
15 and the particle size range of the polymer was
established as 40 - 900 microns with a means of 81.1
microns. The composition contained less than 9%
emulsion, i.e. of beads less than 10 μ m.

20 Example 8

Example 7 was repeated but in a flat bottom vessel
with a stirrer speed of 300rpm and using lauryl peroxide
as the initiator. The particle size range was from 20-
200 microns, with a mean particle size of 79 microns.
25 The composition contained less than 8% emulsion.

Example 9

Example 7 was repeated by varying the amount of

hydrophobic monomer blend charged to the reactor so as to provide reaction solids of 30%, 35% and 40%. The results are as follows:-

5	Solids	Particle Size Range of Beads	Emulsion
	30%	40-350 microns	27.7%
	40%	10-200 microns	24.6%

Example 10

10 Example 7 was repeated at 25% solids content but varying the amounts of stabiliser, defoamer and cationic monomer.

	% Stabiliser	Additions	Particle Size Range	Emulsion
15	10% PVA	2% Lauryl bromide quaternised dimethyl aminoethyl methacrylate dimethyl	V.thick bimodal 6-200 microns	not measured
	5% PVA	2% Arquad T-30	Small lumps aggregated beads	not measured
	5% PVA	2% Disponil A3065	V.Broad distribution	not measured
	10% PVA	1% NaCl and 5% Methyl end capped PEG 2000	40-400 microns	46.3%
	10% PVA	1% NaCl 5% MPEG 1000	Bimodal 40-400 microns	not measured
20	10% PVA	1% NaCl 10% MPEG 2000	40-150 microns	36.8%
	10% PVA	1% NaCl 5% Methyl end capped PEG 2000 2% Synperonic PE/L61	40-400 microns	43.2%

Example 11

Example 7 was repeated using an amount of
25 hydrophobic monomer that would provide a reaction medium

of 25% solids and different grades of polyvinyl alcohol were used having different degrees of hydrolysis. In one test sodium chloride was added to the aqueous phase and the tests using 98% hydrolysed PVA, lauryl bromide

5 quaternised dimethylaminoethyl methacrylate was used in place of the benzyl chloride quaternary cationic monomer.

	% Stabiliser	Stabiliser type	Additions	Results
	10%	88% hydrolysed (high mol wt)		100-200 microns
10	10%	73% hydrolysed		100-200 microns
	10%	88% hydrolysed (high mol wt)	1% NaCl	Large beads formed
	5%	98% hydrolysed	0.15% Lauryl Bromide Quat	Polymer turned solid
	5% A-300	98% hydrolysed	0.2% Lauryl Bromide Quat	Large beads formed
	10% A-300	98% hydrolysed	0.5% Lauryl Bromide Quat	Very small beads formed

15

Example 12

Example 7 was repeated but using different levels of stabiliser.

20	% Stabiliser	Results
	15%	0.2 - 150 microns, mean 13 microns
	10%	20 - 400 microns, mean 109 microns
	7.5%	20 - 400 microns, mean 122 microns
	5%	20 - 900 microns, mean 105 microns
25	2.5%	60 - 800 microns, mean 222 microns

Example 13

Example 7 was repeated using the following cationic monomers:-

5	Product	Cationic Monomer Used
	A	tertiary butyl aminoethylmethacrylate (TBAEMA)
	B	Methyl chloride quaternised DMAEMA (MBJ)
	C	Dimethyl aminopropyl methacrylamide (DAPMA)
10	D	Benzyl chloride quaternised DMAEMA (MADQUAT BZ 75)

In performance tests the products A-D were dispersed into a perfume base having a cationic character to assess whether the particles form agglomerates. Products A and
15 B formed agglomerates, product C formed some agglomerates but D was almost free of agglomerates.

Example 14

Example 7 was repeated using DAPMA acetate salts, with
20 different degrees of neutralisation, as the cationic monomer component. The amount of emulsion produced was measured.

	Additions	Results	Emulsion
	2% DMAPMA 100% neutralised	pH 5.42	33%
5	2% DMAPMA 75% neutralised	pH 8.0	28.7%
	2% DMAPMA 50% neutralised	pH 8.4	18.9%
10	2% DMAPMA 25% neutralised	pH 8.6	19.6%

Example 15

Example 7 was repeated but using various levels of benzyl
 15 chloride quaternised dimethylaminoethyl methacrylate.

	Amount of cationic monomer	Performance test in perfume base	Emulsion
	1.0%	no agglomerates occurred	16.2%
20	0.5%	no agglomerates occurred	13.0%
	0.2%	virtually none	17.9%
	0.1%	formed small white agglomerates	15.8%

25 Example 16

The polymer particles produced in Example 7 evaluated by
 assessing the ability to absorb water insoluble active
 ingredients. 10 parts of beads were dispersed into 10
 parts of liquid water insoluble active ingredients and
 30 the quantity of liquid absorbed was observed visually.

	Active	Description	Volume pre Absorption	% Absorption
	Propischlor	Herbicide	1	0
	Gossyplure	Semio Chemical	1.2	100
5	Methyl Eugenol	Semio Chemical	1	100
	Trimedlure	Semio Chemical	1	50
	Spiroketal	Semio Chemical	1	100
10	Pyrethrum Extract 25% Active in parraffinic solvent	Insecticide	1	20
	Pyrethrum Extract 50% Active	Insecticide	1.1	50
	Ethion	Insecticide	1	50
15	Cypermethrin 50% Active in Solvesso 200 solvent	Insecticide	2	50
	Furfural	Soil Sterilant	1	100

20 Example 17

A preparation of isobutyl methacrylate polymer was repeated with differing quantities of MADQUAT as the only variable. The results show that mean particle size increases with quantity of such a cationic monomer.

25	% MADQUAT	Mean particle size, μm
	0.22	74
	0.3	98
	0.4	109
30	0.5	165

CLAIMS:

1. Water-insoluble particles formed of a core polymer of (meth)acrylic monomer with at least three carbon atoms in the esterifying alcohol and having at their surface a further polymer with free hydroxyl functionality.
2. Water-insoluble particles formed of hydrophobic core polymer and having at their surface at least one further polymer which contribute(s) a hydroxyl and a cationic functionality at that surface.
3. Polymeric particles according to claim 1 or claim 2 wherein the particles have an average particle size of at least 40 microns but no more than 150 microns.
4. Polymeric particles according to any preceding claim wherein the further polymer(s) containing free hydroxy groups also contain(s) pendant cationic groups.
5. Polymeric particles according to any preceding claim wherein cationic functionality at the surface is provided by one or more cationic vinyl addition monomers selected from quaternised salts of dimethyl amino propyl acrylamide and dimethyl amino propyl methacrylamide.
6. Polymeric particles according to any preceding claim wherein cationic functionality at the surface is provided

by one or more cationic vinyl addition monomers selected from C₄-C₈ alkyl, aryl, alkaryl, aralkyl halide of dimethyl amino (meth)acrylates.

- 5 7. Polymeric particles according to any preceding claims wherein cationic functionality at the surface is provided by a benzyl-chloride-quaternised dimethyl amino ethyl methacrylate monomer.
- 10 8. Polymeric particles according to any preceding claim wherein the core polymer is based on alkyl esters of acrylic acid or methacrylic acid.
9. Polymeric particles according to any preceding
15 claims wherein the core polymer is based on alkyl ester of acrylic acid or methacrylic acid and a multifunctional cross-linking monomer.
10. Polymeric particles according to any preceding claim
20 wherein the core polymer is based on isobutyl methacrylate and divinyl benzene.
11. Polymeric particles according to any preceding claim wherein the further polymer providing hydroxy
25 functionality is selected from polymers comprising vinyl alcohol units.
12. Polymeric particles according to any preceding claim

wherein the polymer providing hydroxy functionality is selected from polyvinyl alcohol comprising at least 80% vinyl alcohol units.

5 13. Polymeric particles according to any preceding claim wherein the polymer providing hydroxy functionality is selected from polyvinyl alcohol comprising at least 85% vinyl alcohol units.

10 14. Polymeric particles according to any preceding claims comprising an active ingredient to be released in a controlled manner, wherein the active ingredient is selected from insecticides, curing agents and sunscreen agents.

15

15. Polymeric particles according to any preceding claim which form stable dispersions in liquid medium containing active ingredients and remain substantially free from agglomerated particles.

20

16. Polymeric particles according to claim 15 which are capable of imbibing and entrapping the active ingredient, whilst remaining in suspension and substantially free from agglomerated particles.

25

17. A method of preparing polymeric products according to any preceding claim by suspension polymerisation of hydrophobic monomers or monomer blend in an aqueous

medium comprising a vinyl addition cationic monomer and as a polymerisation stabiliser a polymer comprising free hydroxy groups.

5 18. A method of preparing polymer products according to any preceding claims by suspension polymerisation of a blend of isobutylmethacrylate and dimethyl benzene in an aqueous medium comprising benzyl chloride quaternised dimethyl amino ethyl acrylate and as a polymerisation
10 stabiliser a polyvinyl alcohol.

19. A method of preparing polymer particles according to claim 17 or claim 18 wherein the suspension polymerisation process is effected by azo or peroxide
15 initiators.

20. A method of preparing polymer particles according to any preceding claim wherein the cationic vinyl addition polymer is a benzyl chloride quaternised dimethyl amino
20 ethyl (meth)acrylate and the resulting polymer particles which have an average particle size in the range 10 microns to 150 microns.

21. A method of preparing polymer particles according to
25 any preceding claim wherein less than 4% of the hydrophobic monomer forms polymer particles of particle size less than 10 microns.

22. A method of preparing polymer particles according to any preceding claim wherein less than 3% of the hydrophobic monomer forms polymer particles of particle size less than 10 microns.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/03531

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F2/20 C11D17/00 A01N25/10

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C11D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 441 512 A (NIPPON CATALYTIC CHEM IND) 14 August 1991 see page 18, line 53 - page 19, line 35; examples 1-5,23 ---	1,8,9, 11-13
X	EP 0 604 109 A (ROHM & HAAS) 29 June 1994 see claims; examples ---	17
X	WO 93 22417 A (UNILEVER PLC ;UNILEVER NV (NL)) 11 November 1993 see polymer 6 see page 22, line 19 - line 21; claims 1-7; example 1; table 1 ---	1,11-13
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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